

* NOTICES *

JP 01-006024

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] It has the stratified deformation organization formed by adding plastic deformation to start material. The layer (2) of one of the aforementioned stratified deformation organizations It consists of the alloy or compound containing the element of at least one sort of groups of the element of 2A group, 3A group, and the 4A groups or 2A group, 3A group, and the 4A groups. Other layers (3) which touch the layer of the above 1 are a hydrogen-absorption material which consists of the alloy or compound containing the element of at least one sort of groups of the element of 6A group, 7A group, and the 8A groups or 6A group, 7A group, and the 8A groups.

[Claim 2] Hydrogen-absorption material according to claim 1 into which at least one main half peak width of a diffraction peak in the X diffraction pattern of the aforementioned stratified deformation organization has the defect density by strong processing to the extent that it becomes width of face of 0.2 degrees or more.

[Claim 3] Hydrogen-absorption material according to claim 1 whose layer thickness of one in the aforementioned stratified deformation organization is 10nm or less.

[Claim 4] The manufacture method of a hydrogen-absorption material equipped with the process which adds strong processing which is characterized by providing the following, and which is accompanied by plastic deformation to start material. One or more sorts of material chosen from the alloy or compound containing the element of at least one sort of groups of the element of 2A group, 3A group, and the 4A groups or 2A group, 3A group, and the 4A groups. One or more sorts of material chosen from the alloy or compound containing the element of at least one sort of groups of the element of 6A group, 7A group, and the 8A groups or 6A group, 7A group, and the 8A groups.

[Claim 5] The manufacture method of a hydrogen-absorption material according to claim 4 of adding strong processing which is made piling up again mutually the material to which strong processing accompanied by plastic deformation was added, and is further accompanied by plastic deformation.

[Claim 6] Strong processing which the aforementioned start material is the gestalt of powder or a pellet, and is accompanied by the aforementioned plastic deformation is the manufacture method of a hydrogen-absorption material according to claim 4 which is mechanical alloying.

[Claim 7] Strong processing accompanied by the aforementioned plastic deformation is the manufacture method of a hydrogen-absorption material according to claim 4 performed by 80% or less of temperature requirement of the melting point of the material chosen as start material.

[Claim 8] The manufacture method of a hydrogen-absorption material according to claim 4 of adding annealing of 80% or less of temperature requirement of the melting point of the material chosen as start material on the occasion of strong processing accompanied by the aforementioned plastic deformation.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

Technical field this invention more specifically relates to the hydrogen-absorption material into which it excelled in hydrogen-absorption capacity, and hydrogen-desorption temperature was reduced, and its manufacture method about hydrogen-absorption material.

Background technology Research and development of hydrogen-absorption material have been actively done with increase of the interest about a hydrogen energy system as a material used for storage of hydrogen, transportation, separation refining of hydrogen gas, energy-conversion equipment, etc. In these research and development, it became clear that there is a problem which hydrogen-absorption material carries out pulverization to repeating absorption and discharge of hydrogen, and collapses. Then, a high material of the resistance over the pulverization which is excellent in hydrogen-absorption capacity, and is produced in connection with the repetition by absorption of hydrogen and discharge was called for strongly. On the other hand, the proposal which recommends the material which has the laminated structure of the thin film which consists of a 4A group metal and a metal of 6A group, 7A group, or 8A group was made (JP,9-59001,A). By considering as the thin film object of such a laminating, the resistance force to the pulverization produced along with absorption and discharge of hydrogen becomes very high. Moreover, in order that 4A group metal which has hcp structure in the state of bulk material may take bcc structure in the laminated structure of a thin film, the position between grids in which hydrogen can be held increases. Since the capacity for bonding strength with hydrogen to be high from the first, and for 4A group metal to absorb hydrogen is high, hydrogen-absorption capacity increases by increase of the kinetic density between grids. Moreover, it follows, and by the material which has the laminated structure of the thin film which consists of the above-mentioned 4A group metal and a metal of 6A group, 7A group, or 8A group, it is hard to carry out pulverization and the material which has very high hydrogen-absorption capacity can be obtained.

However, at the above-mentioned charge of thin film plywood, since 4A group element Ti is included, the weight of the charge of thin film plywood is large, and when mass-producing, the restrictions like resources must be received, and it cannot but become expensive exceeding the price suitable as this kind of an industrial material for utilization. For this reason, search of the element for which 4A group metal can be substituted was performed. Consequently, having the same capacity as 4A group metal was found out in respect of hydrogen-absorption capacity in 2A group and 3A group metal, and the proposal of the charge of hydrogen-absorption plywood which makes 4A group metal substitute for 2A group or 3A group metal was made (Japanese Patent Application No. 11-165890). Mg of the 2A group elements is lightweight also abundantly in resources in weight. For this reason, it was cheap and lightweight and it became possible to obtain the charge of plywood excellent in the hydrogen-absorption capacity which cannot carry out pulverization easily.

Then, the purpose of this invention has so low that hydrogen-absorption capacity does not serve as an obstacle high and serious although a nickel hydrogen rechargeable battery, the fuel cell using hydrogen, the energy conversion system using hydrogen, etc. are easily used for everyday life hydrogen-desorption temperature, and is to specifically provide about 150 degrees C or less with the hydrogen-absorption

material which can be mass-produced, and its manufacturing method low.

Indication of invention The hydrogen-absorption material of this invention includes the stratified deformation organization formed by adding plastic deformation to start material. the layer of one of the stratified deformation organizations It consists of the alloy or compound containing the element of at least one sort of groups of the element of 2A group, 3A group, and the 4A groups or 2A group, 3A group, and the 4A groups. Other layers which touch the layer of 1 consist of the alloy or compound containing the element of at least one sort of groups of the element of 6A group, 7A group, and the 8A groups or 6A group, 7A group, and the 8A groups.

By this stratified deformation organization, contact in the layer of 1 and other layers can make high kinetic density between grids which is secured and becomes easy to include the crystal structure of bcc in the layer of 1 and by which hydrogen is contained. Moreover, since a stratified deformation organization is realized by plastic deformation, defects, such as transposition and a stacking fault, are formed by high density, the trap of the hydrogen is carried out to the defective part, and hydrogen-absorption capacity improves. Furthermore, since a defective part serves as a high-speed diffusion path of hydrogen, hydrogen-desorption temperature falls sharply by formation of a high-density defective part. Since it can moreover manufacture by processing meanses, such as rolling, within a short period of time, it is efficient and the amount of the order of the ton needed on practical use level can be produced.

In addition, as it is indicated in drawing 1 or drawing 2 as a stratified deformation organization, the organization for which the overlapping dissimilar materials add and generate strong processing accompanied by plastic deformation is pointed out, and it is different from the structure shown in drawing 3 known as a laminated structure from the former. In the organization which shows drawing 1, the portion to which each class was equal is turned up at random in the organization which each class has gathered in rolling and the direction of a wire drawing, on the other hand shows drawing 2.

When the quick diffusion in the defective part of a hydrogen atom is thought as important, or when the above-mentioned hydrogen-absorption material is others, at least one main half peak width of a diffraction peak in the X diffraction pattern of a stratified deformation organization has the defect density by strong processing to the extent that it becomes width of face of 0.2 degrees or more.

The half peak width of an X diffraction peak can estimate the density of defects, such as transposition and a stacking fault. Usually, in order to raise the diffusion rate of hydrogen, a half peak width makes 0.2 degrees or more 1 degrees or more as 0.5 degrees or more and most desirable state preferably. The bias of a charge is formed, as a result of being easy to carry out the segregation of the impurity to a defective part and an impurity's segregating. It is thought that the bias of this charge has the operation which draws and carries out the trap of the hydrogen. In order to produce a trap operation of this hydrogen clearly, it is desirable that a half peak width is 0.5 degrees or more. However, it does not say that a half peak width should just spread, and it is not desirable to change into the state where a clear diffraction peak does not arise by amorphous one, i.e., an X diffraction, as a result of strong processing. Since the joint structure in which the crystal structure was formed is cut and the trap of the hydrogen atom is strongly carried out by this cut joint structure, although hydrogen storage capacity increases in the amorphous state, the amount of hydrogen which can be emitted at the temperature of practical use level decreases sharply. In addition, main diffraction peaks point out three high peaks to the 1st - 3rd of the diffraction peaks of the material set as the object of an X diffraction. Moreover, when it is the material in which many diffraction peaks appear, the 3rd is made into the 5th and it is good also as five peaks. A half peak width can be easily read on a chart. However, before the diffraction peak made into the measuring object adds plastic working, a half peak width already excepts 0.2 degrees or more of a certain things. With the alloy which the deposit of a sludge has produced, since there is a diffraction line by which a half peak width becomes 0.2 degrees or more therefore, such a diffraction line is not made into the object of measurement.

When the above-mentioned hydrogen-absorption material securing a latus touch area between the layer of 1 and other layers, and obtaining high-density defect density is thought as important, or in being others, the layer thickness of one in a stratified deformation organization may be 10nm or less.

Making thin the layer of 1 in a stratified deformation organization means strong processing accompanied

by plastic deformation, and it means disappearance (phenomenon in which a hexagonal thing carries out phase transition easily to a cubic) of the idiomorphic operation by lamination, i.e., disappearance of the organization potency force of the crystal structure stable originally, and the high-density defective generation which is formation of the high-speed diffusion path of hydrogen, and a source of a hydrogen trap further. Moreover, a latus touch area is also securable between the layer of 1, and other layers. That is, as an index of high defect density and a latus touch area, the layer thickness of one in a stratified deformation organization can be used. This thickness puts the average thickness of the thickest portion of each class. When two layers of 1 are continuing, it considers that it has dissociated on the front face of one layer of 1, and measures. If this thickness exceeds 10nm, defect density and a touch area are insufficient, hydrogen storage capacity runs short, and hydrogen-desorption temperature becomes high exceeding practical use level. With a transmission electron microscope (transverse electromagnetic), the thin film sample which uses a cross section perpendicular to the processing direction as a front face is extracted, and even if few per one visual field, thickness is measured about ten places and ten visual fields or more, and the average of the layer thickness of 1 is taken out. When the processing direction is the powder which is not clear and which carried out mechanical alloying, it measures with a visual field (10 or more per one visual field, and ten visual fields or more), statistical processing is carried out, and the above-mentioned thickness is taken out.

One or more sorts of material which chose the manufacture method of the hydrogen-absorption material concerning this invention from the alloy or compound containing the element of at least one sort of groups of the element of 2A group, 3A group, and the 4A groups or 2A group, 3A group, and the 4A groups, It has the process which adds strong processing accompanied by plastic deformation to the start material containing one or more sorts of material chosen from the alloy or compound containing the element of at least one sort of groups of the element of 6A group, 7A group, and the 8A groups or 6A group, 7A group, and the 8A groups.

Defects, such as transposition and a stacking fault, are introduced into a crystal lattice by strong processing accompanied by plastic deformation. This transposition, stacking fault, etc. change to the state where the defect became entangled by the increase in the number of times of processing, and it was accumulated. These defect-cluster sections raise the diffusion rate of hydrogen, and function as a high-speed diffusion path of hydrogen. It is furthermore easy to carry out the segregation of the impurity to a defect, and the bias of a charge arises according to the segregation of an impurity. The bias part of a charge makes the hydrogen storage capacity itself increase in order to act as a trap site of a hydrogen atom. Moreover, the touch area of the layer of one in a stratified deformation organization and other layers becomes large by strong processing accompanied by plastic deformation, and it becomes easy to include bcc structure in the layer of 1. If bcc structure is included, the density of the position between grids which contains a hydrogen atom will become high, and hydrogen-absorption capacity will increase.

When raising defect density more than fixed, and making sufficiently thin each composition layer thickness of a stratified deformation organization by the manufacture method of the above-mentioned hydrogen-absorption material is thought as important, or in being others, the material to which strong processing accompanied by plastic deformation was added is made to pile up mutually again, and it considers as start material, and adds strong processing further accompanied by plastic deformation. The above-mentioned method enables it to add big plastic deformation, using material effectively. since it becomes the configuration of a board or a line by the manufacture method of the above-mentioned hydrogen-absorption material -- **** -- in the case of others, when it is hard to form a stratified deformation organization, it is the gestalt of powder or a pellet, and start material encloses into a pipe with ductility, and strong processing is performed as a state of a board or a line, or it carries out strong processing by the mechanical alloying accompanied by plastic deformation. Since a stratified deformation organization is formed to a front face or the interior in the state of powder of mechanical alloying, a preforming object can be produced using this powder and a desired configuration can be processed. Consequently, it becomes possible to obtain the parts which combined high hydrogen-absorption capacity and low hydrogen-desorption temperature without restrictions of a

configuration.

By the manufacture method of the above-mentioned hydrogen-absorption material, when temperature goes up in the middle of plastic deformation and it anneals, strong processing or annealing which is accompanied by plastic deformation by 80% or less of temperature requirement of the melting point of the material chosen as start material in the case of others is added.

If temperature exceeds 80% of the melting point, alloying will advance between different-species layers and the meaning of contact between dissimilar materials will be spoiled. Although it means the melting point of the material which generally has the high melting point among dissimilar materials, the melting point here may be the melting point of low melting point material in order to reduce the driving force of diffusion permeation from a viewpoint which prevents advance of alloying, when a refractory material carries out a diffusion invasion alternatively inside low melting point material. Moreover, if temperature exceeds 80% of the melting point, the density of transposition or a stacking fault decreases, hydrogen-absorption capacity will not decline or the discharge temperature of hydrogen will not fall. In addition, the melting point is displayed by Celsius-degree **, and the above-mentioned temperature requirement puts 80% or less of Celsius-degree ** of the numeric value of the Celsius-degree **.

The best gestalt for inventing (example 1 : strip processing)

First, the example 1 in which the stratified deformation organization which relates to this invention with strip processing was formed is explained. What is shown in example No. of this invention 1-12 of Table 1 was used for one kind in 2A, 3A, and 4A group metal, and one kind in 6A, 7A, and 8A group metal of combination. Although one kind is called layer of others one kind of the layer of 1 and 6A and 7A, and the 8A group metals of 2A, 3A, and the 4A group metals, the layer of 1 and other layers are not necessarily arranged regularly by turns. In the part where the layer of 1 was cut for strong processing, it is not a regular array. In future explanation, L system metal, 6A and 7A, and 8A group metal are called H system metal for 2A, 3A, and 4A group metal. Moreover, what is shown in example No. of this invention 13-17 was used for examples, such as combination of one kind of layer of the L system metals inserted into two kinds of layers of the H system metals. Here, the combination which shows No. 13 in Table 1 will be repeated, and the layers of H system metal will touch on the boundary line of a repeat. In above No. 13-17, example No. of this invention 15 consist of two kinds of layers of L system metal and H system metal, and the Mg-Si compound (silicification magnesium) is used as an L system metal.

Next, the manufacture method of the specimen of example No. of this invention 1-12 is explained. After performing pickling processing to one kind of board of L system metal of 1mm thickness, it annealed in the elevated-temperature vacuum, the scaling film was fully removed, and it considered as the clean surface. You may anneal the process of removal of this scaling film in hydrogen atmosphere or Ar atmosphere, without carrying out only pickling and carrying out pickling. Or machine cutting may remove a scaling film. Next, after performing the same processing to one kind of board of H system metal of 1mm thickness, the scaling film was removed similarly and it considered as the clean surface. Subsequently, it piled up one surface-cleaning-ized board at a time by turns, and the layered product (20mm in nominal thickness) of a total of 20 sheets was produced. The workability of 10% - 50% of rolling reductions per one pass was adopted by having used this layered product as rolling material, and multi-path rolling was performed. Especially heating before rolling was not performed, but a working speed and the time between paths were adjusted so that it might not exceed 300 degrees C by temperature increase by plastic working during strip processing.

When the thickness of a layered product was measured and it was thin to 10mm for every rolling path, it cut in the center section so that the length of a rolling direction might become half, and impurities, such as a surface lubricating oil adhering to the front face of each layered product, were annealed and removed in pickling and the elevated-temperature vacuum. The laminating of these layered products that it was carried out for 2 minutes and defecated the front face was carried out further, and as a rolling material with a nominal thickness of 20mm, again, rolling was obtained in Japanese common chestnut and carried out. The process of this rolling, cutting, surface cleaning-ized processing, and layered product formation ** as a rolling material is repeated 20 times or more a total of 15 times or more depending on a specimen, and it was made to go into the range whose thickness of each class is 1-10nm.

In addition, although it was piled up two sheets this time, having used thickness before piling up as 10mm, even if it is good and piles up two or more sheets also by the thickness more than it or not more than it in fact, it is ineffective to it being the same. When a crack occurred greatly during strip processing, the cure which performs annealing processing and raises processability was performed. however, an annealing temperature is 300 degrees C or less below the temperature in which diffusion does not occur between the layer of L system metal, and the layer of M ** metal

表 1

		材料の組合せ	水素吸蔵量 (H/M)	bcc 構造を示す XRD ピーク	欠陥
本 発 明 例	1	Ti/Cr	3.0	有	有
	2	Ti/Ni	2.5	無	有
	3	Ti/Fe	2.5	有	有
	4	Mg/Cr	2.5	有	有
	5	Mg/Ni	2.5	無	有
	6	Ca・Mg/Cr	2.5	有	有
	7	Y/Ni	3.0	無	有
	8	Y/Cr	2.5	有	有
	9	La/Ni	2.5	無	有
	10	La/Cr	2.5	有	有
	11	Yb/Ni	2.5	有	有
	12	Yb/Cr	2.5	有	有
	13	Cr/Mg/Ni	3.0	有	有
	14	Ti/Mg/Ni	3.0	無	有
	15	Mg-Si/Ni	2.0	有	有
	16	Mg/Cr/Ti	2.5	有	有
	17	Fe/Mg/Cr	2.0	有	有
比 較 例	18	MgNi ₅	1.5	無	無
	19	CaNi ₅	1.0	無	無
	20	LaNi ₅	1.0	無	無
	21	LaCr ₅	0.5	無	無

The point that the layered product as a rolling material consists of three kinds of sheet metal is only different, and production of the specimen of example No. of this invention 13-17 of Table 1 is fundamentally the same as the above-mentioned strip-processing method. However, example No. of this invention 15 consist of two kinds of sheet metal, and one of kinds of it is an Mg-Si compound (silicification magnesium).

The thin film was started from the specimen produced by the above-mentioned method, and it considered as the hydrogen-absorption specimen. Hydrogen-absorption processing was performed to this hydrogen-absorption specimen by the electrolysis charging method. The equipment which performs hydrogen-absorption processing is shown in drawing 4. In performing hydrogen-absorption processing with reference to drawing 4, the specimen 10 was dipped in the NaOH solution of 0.1M, and the Pt counter electrode 12 was dipped in K₂SO₄ solution of 0.5M. To the specimen 10, positive current was passed for negative current predetermined time by the constant current power supply 11 again at the Pt counter electrode 12. ADVANTEST TR6120A was used for this constant current power supply 11. In

addition, current value set to 10mA fundamentally, and set up time to pass current in 1 hour. (Current A) x time (s) was equivalent to quantity of electricity, and calculated the yield of the hydrogen by electrolysis based on Faraday's law using this value. Horiba EMGA621 performed measurement of hydrogen by which occlusion was carried out. This equipment can analyze analysis of the absolute magnitude of hydrogen, or temperature up analysis. Hydrogen storage capacity was specifically calculated by the following methods. First, the temperature up of the specimen is carried out and the fixed quantity of the hydrogen which came out of the specimen is carried out by gas analysis. Then, the specimen from which hydrogen escaped is melted from an acid, and the fixed quantity of the specimen is carried out by the chemical analysis. H/M was calculated from both fixed quantity values. Each used bulk material for the example of comparison.

Moreover, the sample of the board thickness cross section of a board which performed the ultimate-pressure total was started, the thin film was created, and transmission-electron-microscope observation (transverse electromagnetic) was performed. Moreover, it analyzed by taking an X diffraction pattern by the 2theta method about the board thickness cross section. One purpose of taking an X diffraction pattern is for investigating whether when L system metal which has hcp structure takes a stratified deformation organization, it will include a part of bcc structure in bulk material. Another purpose is for high-density defects', such as transposition's introduced by plastic working's, such as strip processing's, and a stacking fault's, remaining in the final state, or measuring and judging the half peak width of a suitable diffraction peak. In Table 1, the judgment of a defect considered as those with defective, when it was able to distinguish clearly, and the half peak width of an X diffraction peak which can belong was measured and there were 1 degrees or more of half peak widths to the sample before carrying out hydrogen-absorption processing, and when it was a 1-degree non-drop, it was displayed that he had no defect.

A test result is shown in Table 1. Each sample of the example of this invention of Table 1 had the stratified deformation organization which shows in the same sample at drawing 1 or drawing 2.

According to transverse-electromagnetic observation, over the direction of board thickness, although the layer of L system metal and the layer thickness of H system metal were not homogeneity, they were thin in the range of 10nm - 1nm thickness. With reference to drawing 1, including the layer 2 of 1 containing L system metallic element, and other layers 3 containing H system metallic element, typically, each class gathered in the processing direction and is prolonged in the stratified deformation organization 1. The layer of 1 and other layers do not necessarily need to be alternations, although there is also a part arranged by turns, and other layers are formed continuously in the fragmentation part 4 of the layer of 1. Similarly, in the fragmentation part 5 of other layers, the layer of 1 is arranged continuously. In some parts of a sample, the portion with the clear processing direction was folded up like drawing 2, and, on the whole, random crystal grain has gathered. Although the organization which shows drawing 2 was accepted in the high part of workability, such as a sample edge, in many cases, it is not necessarily limited to the high part of workability. The stratified deformation organization accepted in the sample of the example of this invention is different from the orderly structure to which the conventional thickness shown in drawing 3 was equal. A laminated structure 101 consists of a layer 102 of 1 to which thickness was equal, and other layers 103 in drawing 3. such, although thickness gathers and is suitable in the set processing direction -- being orderly -- it is not necessarily desirable For example, with the structure shown in drawing 2, since directivity was lost as a whole, the traverse speed of hydrogen improves.

All of example No. of this invention 1-17 showed 2.0 or more H/M. As for H/M, No. 7-12 and No. 15 showed 2.0 or more. Especially, since a high-density defect is included in spite of not including bcc structure, example No. of this invention 2, and 5, 7, 9 and 14 show high H/M. This reason is that it is easy to carry out the segregation of the impurity near the defect, and the bias of a charge arises according to the segregation of an impurity in the near, and the trap of the hydrogen atom is carried out to the bias as described above.

When processing it an oppressive total like an example 1, many defects are introduced during a crystal. The these-introduced defect changes to the state where the defect became entangled by the increase in

the number of processing repetitions. These defects act as a high-speed diffusion path of hydrogen, and it not only raises hydrogen-absorption capacity as mentioned above, but they reduce the discharge temperature of hydrogen. These defect density is estimated by the half peak width of an X diffraction peak. However, since it is thought that transposition cannot exist easily in the crystal grain child, the defect density said here does not necessarily express only dislocation density with the fine crystal material of nano meter order. In order to increase the diffusion rate of hydrogen, a half peak width may be 0.2 degrees or more. In order to make hydrogen storage capacity increase furthermore, it is desirable to have the half peak width of 0.5 degrees or more. Since each example of this invention displayed on Table 1 as those with defective has the half peak width of 1 degrees or more, it has contributed to improvement in H/M greatly.

Moreover, about example No. of this invention 5 (Mg/nickel (mole ratio 2:1 of Mg and nickel)) of Table 1, above-mentioned Horiba EMGA621 performed temperature up analysis, hydrogen-desorption speed was found on 10 degrees-C heating conditions for /of programming rates, and it compared with Mg2nickel of bulk material. Discharge of hydrogen was accepted from 50 degrees C, and discharge speed became the maximum at 100 degrees C example No. of this invention 5. On the other hand, as for Mg2nickel of bulk material, discharge of hydrogen was performed in 200-300 degrees C. Therefore, the hydrogen-absorption material concerning this invention becomes possible [being used for the hydrogen source of supply for a nickel hydrogen rechargeable battery or fuel cells practical] by adding strong processing to which the half peak width of an X diffraction peak becomes 1 degrees or more as mentioned above, and raising defect density. Unlike the manufacture method by the ion plating method, the manufacture method by this rolling is suitable for mass production method, and it is possible to manufacture the hydrogen-absorption material concerning this invention of ton order on the basis of high productivity.

(Example 2 : wire drawing)

First, the example 2 in which the stratified deformation organization which relates to this invention by wire drawing was formed is explained. What is shown in example No. of this invention 1-12 of Table 2 was used for one kind of L system metal, and H system metal [one kind of] combination. Moreover, what is shown in example No. of this invention 13-17 was used for examples, such as two kinds in H system metal, and one kind in L system metal of combination. However, example No. of this invention 15 consist of two kinds of sheet metal of L system metal and H system metal, and the Mg-Si compound (silicification magnesium) is used as an L system metal.

表 2

		材料の 組合せ	組成比 (モル比)	水素吸蔵量 (H/M)	bcc 構造を示す XRD ピーク	欠陥
本 発 明 例	1	Ti/Cr	1:1	3.0	有	有
	2	Ti/Ni	2:1	2.5	無	有
	3	Ti/Fe	1:1	2.5	有	有
	4	Mg/Cr	2:1	2.5	有	有
	5	Mg/Ni	2:1	2.5	無	有
	6	Ca-Mg/Cr	1:1:2	2.5	有	有
	7	Y/Ni	1:1	2.0	無	有
	8	Y/Cr	1:1	2.5	有	有
	9	La/Ni	1:1	2.5	無	有
	10	La/Cr	1:1	2.5	有	有
	11	Yb/Ni	2:1	2.5	有	有
	12	Yb/Cr	2:1	2.5	有	有
	13	Cr/Mg/Ni	1:2:1	2.0	有	有
	14	Ti/Mg/Ni	1:1:1	2.0	無	有
	15	Mg-Si/Ni	2:1:1	2.0	有	有
	16	Mg/Cr/Ti	1:1:2	2.5	有	有
	17	Fe/Mg/Cr	1:1:1	2.0	有	有
比 較 例	18	MgNi ₅	- - - -	1.5	無	無
	19	CaNi ₅	- - - -	1.0	無	無
	20	LaNi ₅	- - - -	1.0	無	無
	21	LaCr ₅	- - - -	0.5	無	無

Next, the manufacture method of the specimen of example No. of this invention 1-12 of Table 2 is explained. The powder of L system metal and H system metal was packed into the copper pipe with an outer diameter [of 20mm], and a bore of 16mm, after adjusting to each mole ratio shown in Table 2 and mixing sufficiently uniformly. The size of the path of each powder was set to 1mm or less. As for the size of this powder, it is desirable to be referred to as 50 micrometers or less. Then, the terminal of a copper pipe was closed and wire drawing was performed. although the roller die performed wire drawing -- swaging and a hole -- it is based on a dice -- it draws out or is possible also by rolling 5% - 30% of within the limits performed the degree of wire drawing by the reduction of area per one pass, and the total reduction of area could be 96% or more. This total reduction of area may be 99.5% or more preferably. If heat treatment of 300 degrees C or less is performed in the middle of wire drawing, it will be easier to process it, and the adhesion of powder will go up, and density will improve. Chemical preparation or machining removed the copper of the front face of a wire after processing, and the wire of the mixture of L system metal and H system metal was obtained. These wires were started and the hydrogen test object which measures hydrogen-absorption ability H/M was extracted. Moreover, two or more wires were summarized, the cross section was started, and the specimen for X diffractions which embedded to the resin and was ground was produced. The measuring method and X-ray diffraction method of H/M were performed like the example 1.

According to the test result shown in Table 2, the example of this invention showed the value with as high H/M as [or more] 2.0. In these, in spite of not including bcc structure in the layer of L system metal, No.2, and 5, 7, 9 and 14 are a high H/M value. This originates in high defect density, as the example 1 was explained in full detail. That is, in the example of this invention, since the half peak

width of an X diffraction peak is 1 degrees or more, transposition, the stacking fault, etc. are formed by high density. On the other hand, it is a pulverization plain-gauze cone by the repetition cycle of absorption of hydrogen and discharge since H/M is within the limits of 0.5-1.5 by the bulk material of No.18-21 of the example of comparison and it is moreover bulk material.

In order to grasp the influence affect the above-mentioned hydrogen-desorption temperature of high defect density, hydrogen desorption was investigated about example No. of this invention 5 of Table 2. Search procedure is as having indicated in the example 1. Consequently, example No. of this invention 5 of Table 2 began hydrogen desorption from 50 degrees C, and it made them clear that the discharge speed maximum at 100 degrees C is shown. On the other hand, as for Mg2nickel of bulk material, discharge of hydrogen was performed in 200-300 degrees C. Therefore, it turns out that a high-density defect is introduced into hydrogen-absorption material by wire drawing, and hydrogen-desorption temperature is reduced by 100-200 degrees C by it. Consequently, it becomes possible to use it as a hydrogen source of supply for the electrodes and fuel cells of the nickel hydrogen rechargeable battery used for elegance every day. These wires are made into the shape of a sheet with-like [wire] etc., and are used for the electrode of a nickel hydrogen rechargeable battery etc. According to the above-mentioned wire drawing, the hydrogen-absorption material of this invention of ton order can be manufactured under high productivity.

(Example 3 : mechanical alloying)

Mg pellet, nickel carbo nil powder, and metal chromium powder were used as the raw material, and mechanical alloying (MA) was beforehand carried out for 500 hours with the planet ball mill with which Ar gas was enclosed after preliminary mixture by the V type mixer at a rate of the last composition ratio. After preforming the obtained powder by the pressure of 500MPa(s) using metal mold and heating it at 300 more degrees C, extruding was immediately carried out by the extrusion ratio 10:1, and a cylindrical material was obtained. In the gestalt 3 of this operation, a stratified deformation organization is formed in the surface section of each powder in the stage of mechanical alloying, it is further lengthened by extruding, each powder extended in the direction of extrusion overlaps, and the stratified deformation organization is formed. In addition, since it is 651 degrees C of melting points of Mg, 1450 degrees C of melting points of nickel, and 1890 degrees C of melting points of Cr, the above-mentioned heating temperature of 300 degrees C has been enough settled in 80% or less of the melting point of each material. That is, the 80 above-mentioned% of temperature is 520.8 degrees C about Mg, and the heating temperature of 300 degrees C is a low from this temperature.

The hydrogen test object was extracted from the above-mentioned cylindrical material, and H/M and hydrogen-desorption temperature were measured by the same method as an example 1. H/M of the specimen of this example 3 was 2.5. Moreover, hydrogen desorption began from near 50 degree C, discharge speed became the maximum in 80 degrees C - 100 degrees C, and when 100 degrees C was reached, about 80% of the hydrogen which carried out occlusion was emitted. Moreover, since powder was left beforehand and it had turned minutely, even if the repetition of the occlusion of hydrogen and discharge was performed, detailed-ization of hydrogen-absorption material did not advance notably.

(Example 4: cyclic press)

By being made from Mg sheet metal, nickel sheet metal, and Cr sheet metal, the size was arranged combining each sheet metal and it carried out semipermanent [of the edge] by spot welding after cutting so that the last composition ratio might be formed beforehand. then, simple -- metal mold -- after having pressurized by welding-pressure 800MPa in inside, carrying out the obtained layered product for 2 minutes and defecating a front face, it piled up again and pressurized The cycle of formation ** of the layered product as this pressurization, cutting, surface-cleaning-izing, and a press work material was repeated 1000 times, and the stratified deformation organization was obtained.

Hardening of material began from the hit exceeding 200 times by this cyclic pressing method. Then, the material which repeated the press 1000 times was held at 500 degrees C in hydrogen of 99.99% of purity for 24 hours, and the oxygen in material was removed. Although the hydrogen storage capacity of the obtained material was 3.0 in H/M, hydrogen absorption temperature and hydrogen-desorption temperature fell within the range of 100 degrees C from the room temperature, and the burst size to the

amount of occlusion was 80% or more. As a result of an affinity with hydrogen putting strong Mg with the material from which the crystal structures, such as nickel and Cr, differ as a reason which the absorption temperature and discharge temperature of hydrogen were able to **** within the limits of 100 degrees C from the room temperature, a big grid strain occurs in the crystal lattice in Mg, and it thinks because the bond distance of hydrogen and Mg was extended. In addition, the heating temperature of 500 degrees C in the above-mentioned hydrogen annealing is a low from 80% of temperature of 520.8 degrees C of 651 degrees C of melting points of Mg.

(Example 5)

To the same material for processing as an example 4 (start material), it rolled out at 20% of rolling reductions with the roll pressure total machine, and it layered-product-formed and cutting, surface-cleaning-izing, and ***** that goes away were repeated 1000 times. The obtained sample was heated at 500 degrees C in hydrogen of 99.99% of purity, and was held for 24 hours, and the oxygen in a sample was removed. As for the hydrogen storage capacity of this sample, the value with as high H/M as 2.5 was acquired. Hydrogen absorption temperature and hydrogen-desorption temperature fell within the range of 90 degrees C from the room temperature, and the burst size to the amount of occlusion was 85% or more.

As a result of inserting Mg with a strong affinity with hydrogen with the material from which nickel, and Mg and the crystal structure of Cr differ as a reason which was able to make the absorption temperature and discharge temperature of hydrogen within the limits of 90 degrees C from the room temperature, a big grid strain occurs in the crystal lattice of Mg, and it thinks because the bond distance of hydrogen and Mg is extended. Since directivity arises in processing especially in a roll pressure total, it may be extended by the crystal lattice of Mg in the processing direction.

By this invention, the hydrogen-absorption material to which it has high hydrogen-absorption capacity by methods, such as strip processing which can be mass-produced, and hydrogen-desorption temperature fell to about 100 degrees C can be offered. Consequently, the large-scale use in related industries including energy, such as energy conversion system which used the electrode material of the nickel hydrogen rechargeable battery for an automobile drive using the low hydrogen-absorption material of hydrogen-desorption temperature, a fuel cell, and hydrogen so much, is attained.

In the above, although the example of this invention was explained, the example indicated above is instantiation to the last, and the range of this invention is not limited to these examples. The range of this invention is shown by the publication of a claim, and includes the publication of a claim, an equal meaning, and all change in within the limits further.

[Brief Description of the Drawings]

Drawing 1 is the ** type view showing one stratified deformation organization accepted in the hydrogen-absorption material of this invention.

Drawing 2 is the ** type view showing other stratified deformation organizations accepted in the hydrogen-absorption material of this invention.

Drawing 3 is the ** type view showing the conventional laminated structure.

Drawing 4 is the ** type view showing the composition of the equipment which realizes hydrogen-absorption processing.

[Translation done.]

(19) 日本国特許庁 (J P)

再 公 表 特 許 (A 1)

(11) 国際公開番号

W O O 1 / 0 0 6 0 2 4

発行日 平成15年2月12日(2003.2.12)

(43) 国際公開日 平成13年1月25日(2001.1.25)

(51) IntCl.⁷ 識別記号
 C 2 2 C 1/00
 C 0 1 B 3/00
 C 2 3 C 14/14
 // B 0 1 J 2/02
 B 2 2 F 5/00

F I
 C 2 2 C 1/00 N
 C 0 1 B 3/00 B
 C 2 3 C 14/14 D
 B 0 1 J 2/02 B
 B 2 2 F 5/00 K

審査請求 未請求 予備審査請求 未請求(全 22 頁) 最終頁に続く

出願番号 特願2001-511231(P2001-511231)
 (21) 国際出願番号 PCT/J P 0 0 / 0 3 7 1 0
 (22) 国際出願日 平成12年6月7日(2000.6.7)
 (31) 優先権主張番号 特願平11-203360
 (32) 優先日 平成11年7月16日(1999.7.16)
 (33) 優先権主張国 日本 (J P)
 (81) 指定国 EP(AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, I T, LU, MC, NL, PT, SE), CA, J P, U S

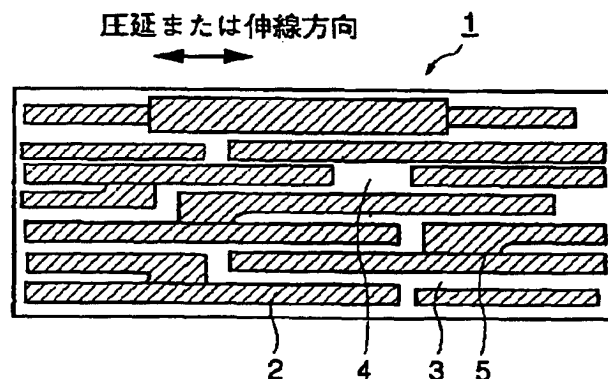
(71) 出願人 住友電気工業株式会社
 大阪府大阪市中央区北浜四丁目5番33号
 (72) 発明者 河部 望
 兵庫県伊丹市昆陽北一丁目1番1号 住友
 電気工業株式会社 伊丹製作所内
 (72) 発明者 曾我部 浩一
 兵庫県伊丹市昆陽北一丁目1番1号 住友
 電気工業株式会社 伊丹製作所内
 (72) 発明者 山中 正策
 兵庫県伊丹市昆陽北一丁目1番1号 住友
 電気工業株式会社 伊丹製作所内
 (74) 代理人 弁理士 深見 久郎 (外4名)

最終頁に続く

(54) 【発明の名称】 水素吸蔵材料およびその製造方法

(57) 【要約】

水素吸蔵能力に優れ、水素放出温度が利用に大きな障害とならないほど低く、かつ大量生産が可能な水素吸蔵材料(1)およびその製造法が得られる。塑性変形を伴う層状変形組織を有し、層状変形組織のうちの一の層(2)は、2A族、3A族、4A族の元素、または2A族、3A族、4A族の少なくとも1種の族の元素を含む合金もしくは化合物よりなっており、一の層に接する他の層(3)は、6A族、7A族、8A族の元素、または6A族、7A族、8A族の少なくとも1種の族の元素を含む合金もしくは化合物よりなっている。



【特許請求の範囲】

【請求項 1】 出発材料に対して塑性変形が加えられることにより形成された層状変形組織を有し、

前記層状変形組織のうちの一の層 (2) は、2 A 族、3 A 族および 4 A 族のうちの元素、または 2 A 族、3 A 族および 4 A 族のうちの少なくとも 1 種の族の元素を含む合金もしくは化合物よりなっており、

前記一の層に接する他の層 (3) は、6 A 族、7 A 族および 8 A 族のうちの元素、または 6 A 族、7 A 族および 8 A 族のうちの少なくとも 1 種の族の元素を含む合金もしくは化合物よりなっている、水素吸蔵材料。

【請求項 2】 前記層状変形組織の X 線回折パターンにおける主要な回折ピークの少なくとも 1 つの半価幅が、 0.2° 以上の幅となるほどの強加工による欠陥密度を有する、請求項 1 に記載の水素吸蔵材料。

【請求項 3】 前記層状変形組織のなかの一の層の厚さが 10 nm 以下である、請求項 1 に記載の水素吸蔵材料。

【請求項 4】 2 A 族、3 A 族および 4 A 族のうちの元素、または 2 A 族、3 A 族および 4 A 族のうちの少なくとも 1 種の族の元素を含む合金もしくは化合物から選んだ 1 種以上の材料と、

6 A 族、7 A 族および 8 A 族のうちの元素、または 6 A 族、7 A 族および 8 A 族のうちの少なくとも 1 種の族の元素を含む合金もしくは化合物から選んだ 1 種以上の材料とを含む出発材料に対して塑性変形を伴う強加工を加える工程を備える、水素吸蔵材料の製造方法。

【請求項 5】 塑性変形を伴う強加工が加えられた材料を再度重ね合わせてさらに塑性変形を伴う強加工を加える、請求項 4 に記載の水素吸蔵材料の製造方法。

【請求項 6】 前記出発材料は粉末またはペレットの形態であり、前記塑性変形を伴う強加工はメカニカルアロイングである、請求項 4 に記載の水素吸蔵材料の製造方法。

【請求項 7】 前記塑性変形を伴う強加工は、出発材料に選んだ材料の融点の 80 % 以下の温度範囲で行われる、請求項 4 に記載の水素吸蔵材料の製造方法。

【請求項 8】 前記塑性変形を伴う強加工に際して、出発材料に選んだ材料の融点

の 8 0 % 以下の温度範囲の焼鈍を加える、請求項 4 に記載の水素吸蔵材料の製造方法。

【発明の詳細な説明】

技術分野

本発明は、水素吸蔵材料に関し、より具体的には水素吸蔵能力に優れ、かつ水素放出温度を低下させた水素吸蔵材料およびその製造方法に関する。

背景技術

水素エネルギーシステムへの関心の増大にともない、水素の貯蔵や輸送、水素ガスの分離精製、エネルギー変換装置などに用いられる材料として、水素吸蔵材料の研究開発が活発に行われてきた。これらの研究開発において、水素の吸収と放出を繰り返すと水素吸蔵材料は微粉化して崩れてしまう問題があることが判明した。そこで、水素吸蔵能力に優れ、かつ水素の吸収と放出とのくり返しに伴って生じる微粉化に対する抵抗性の高い材料が強く求められた。これに対して、4 A族金属と6 A族、7 A族、8 A族のいずれかの金属とからなる薄膜の積層構造を有する材料を推奨する提案がなされた（特開平9-59001号公報）。このような積層の薄膜体とすることにより、水素の吸収と放出に付随して生じる微粉化に対する抵抗力は非常に高くなる。また、バルク材の状態でh c p構造を有する4 A族金属は薄膜の積層構造ではb c c構造をとるため、水素を收容しうる格子間位置が増大する。4 A族金属はもともと水素との結合力が高く水素を吸収する能力は高いので、格子間位置密度の増大により、水素吸蔵能力が増大する。また、したがって、上記の4 A族金属と6 A族、7 A族、8 A族のいずれかの金属とからなる薄膜の積層構造を有する材料により、微粉化しにくく、非常に高い水素吸蔵能力を有する材料を得ることができる。

しかしながら、上記の薄膜積層材料では4 A族元素T iを含むので、薄膜積層材料の重量が大きく、また大量生産する場合に資源的な制約を受け、この種の工業材料としては実用化に適当な価格を超えて高価にならざるを得ない。このため、4 A族金属に代替可能な元素の探索が行われた。その結果、2 A族および3 A族金属が水素吸蔵能力という点で4 A族金属と同様な能力を有することが見出され、4 A族金属に2 A族または3 A族金属を代替させる水素吸蔵積層材料の提案がなされた（特願平11-165890）。2 A族元素のうちの、例えばM gは資源的に豊富であり、また重量的にも軽量である。このため、安価かつ軽量で微

粉化しにくい水素吸蔵能力に優れた積層材料を得ることが可能になった。

そこで、本発明の目的は、水素吸蔵能力が高く、ニッケル水素２次電池、水素を利用した燃料電池、水素を利用するエネルギー変換システム等を日常生活に容易に利用するのに大きな障害とならないほど水素放出温度が低く、具体的には１５０℃以下程度に低く、かつ大量生産が可能な水素吸蔵材料およびその製造法を提供することにある。

発明の開示

本発明の水素吸蔵材料は、出発材料に対して塑性変形が加えられることにより形成された層状変形組織を含み、層状変形組織のうちの一の層は、２Ａ族、３Ａ族および４Ａ族のうちの元素、または２Ａ族、３Ａ族および４Ａ族のうちの少なくとも１種の族の元素を含む合金もしくは化合物よりなっており、一の層に接する他の層は、６Ａ族、７Ａ族および８Ａ族のうちの元素、または６Ａ族、７Ａ族および８Ａ族のうちの少なくとも１種の族の元素を含む合金もしくは化合物よりなっている。

この層状変形組織により、一の層と他の層との接触は確保され一の層にbccの結晶構造を含みやすくなり水素が収納される格子間位置密度を高くすることができる。また、塑性変形により層状変形組織が実現されるので、転位や積層欠陥等の欠陥が高密度で形成され、その欠陥部に水素がトラップされ、水素吸蔵能力が向上する。さらに、欠陥部は水素の高速拡散経路となるので、高密度の欠陥部の形成により水素放出温度は大幅に低下する。その上、圧延等の加工手段により製造することができるので、実用レベルで必要とされるトンのオーダーの量を短期間のうちに高効率で生産することができる。

なお、層状変形組織とは、図１または図２に示すように、重なり合った異種材料が塑性変形を伴う強加工を加えられて生成する組織を指し、従来から積層構造として知られている図３に示す構造とは相違する。図１に示す組織では、各層は圧延、伸線方向に揃っており、これに対して、図２に示す組織では、各層が揃った部分がランダムに折り重ねられている。

上記の水素吸蔵材料は、水素原子の欠陥部における速い拡散が重視される場合またはその他の場合には、層状変形組織のX線回折パターンにおける主要な回折

ピークの少なくとも1つの半価幅は、 0.2° 以上の幅となるほどの強加工による欠陥密度を有する。

転位や積層欠陥等の欠陥の密度は、X線回折ピークの半価幅によって評価できる。通常、水素の拡散速度を高めるためには、半価幅は 0.2° 以上、好ましくは 0.5° 以上、最も好ましい状態としては 1° 以上とする。欠陥部には不純物が偏析しやすく、不純物が偏析した結果、電荷の偏りが形成される。この電荷の偏りは水素を引きつけトラップする作用を有すると考えられる。この水素のトラップ作用を明瞭に生じさせるためには、半価幅が 0.5° 以上であることが好ましい。しかしながら、半価幅は広がればよいというものではなく、強加工の結果、アモルファス、すなわちX線回折により明確な回折ピークが生じない状態にまでにすることは好ましくない。アモルファス状態では、結晶構造を形成していた結合構造が切断され、この切断された結合構造により水素原子は強くトラップされるので、水素吸蔵量は増加するが、実用レベルの温度で放出可能な水素量が大幅に減少する。なお、主要な回折ピークとはX線回折の対象となっている材料の回折ピークのうち第1番目～第3番目に高い3つのピークを指す。また、回折ピークが多数現れる材料の場合には、第3番目を第5番目として5つのピークとしてもよい。半価幅はチャート上で容易に読み取ることができる。ただし、測定対象とする回折ピークは塑性加工を加える前に既に半価幅が 0.2° 以上あるものは除外する。析出物の析出が生じている合金等では、半価幅が 0.2° 以上となる回折線があるので、したがって、このような回折線は測定の対象としない。

上記の水素吸蔵材料は、一の層と他の層との間に広い接触面積を確保しかつ高密度の欠陥密度を得ることが重視される場合またはその他の場合には、層状変形組織のなかの一の層の厚さは10 nm以下とする。

層状変形組織における一の層を薄くすることは、塑性変形を伴う強加工を意味し、薄層化による自形作用の消失、すなわち、本来安定な結晶構造の形成能力の消失（六方晶のものが立方晶へと容易に相転移する現象等）や、さらに水素の高速拡散パスの形成や水素トラップ源である高密度の欠陥生成を意味する。また、一の層と他の層との間に広い接触面積を確保することもできる。すなわち高い欠陥密度および広い接触面積の指標として、層状変形組織のなかの一の層の厚さを

用いることができる。この厚さは各層の最も厚い部分の平均的な厚さをさす。2つの一の層が連続しているような場合は、一方の一の層の表面で分離しているとみなして測定する。この厚さが10 nmを超えると欠陥密度および接触面積が不足して、水素吸蔵量が不足し、水素放出温度が実用レベルを超えて高くなる。加工方向に垂直な断面を表面とする薄膜試料を採取して、透過電子顕微鏡(TEM)により、1視野あたり少なくとも10箇所、10視野以上について厚さを測定し、一の層の厚さの平均値を出す。加工方向が明確でないメカニカルアロイングした粉末の場合は、1視野あたり10ヶ所以上、10視野以上の視野で測定して統計的な処理をして上記の厚さを出す。

本発明に係る水素吸蔵材料の製造方法は、2A族、3A族および4A族のうちの元素、または2A族、3A族および4A族のうちの少なくとも1種の族の元素を含む合金もしくは化合物から選んだ1種以上の材料と、6A族、7A族および8A族のうちの元素、または6A族、7A族および8A族のうちの少なくとも1種の族の元素を含む合金もしくは化合物から選んだ1種以上の材料とを含む出発材料に対して塑性変形を伴う強加工を加える工程を備える。

塑性変形を伴う強加工により、結晶格子に転位や積層欠陥等の欠陥が導入される。この転位や積層欠陥等は、加工回数の増加により欠陥が絡み合って集積した状態へと変化する。これらの欠陥集積部は、水素の拡散速度を向上させ、水素の高速拡散経路として機能する。さらに欠陥には不純物が偏析しやすく、不純物の偏析により電荷の偏りが生じる。電荷の偏り箇所は水素原子のトラップサイトとして作用するため、水素吸蔵量そのものを増加させる。また、塑性変形を伴う強加工により層状変形組織のなかの一の層と他の層との接触面積は広くなり、一の層にbcc構造を含みやすくなる。bcc構造が含まれると、水素原子を収納する格子間位置の密度が高くなり水素吸蔵能力が増大する。

上記の水素吸蔵材料の製造方法では、欠陥密度を一定以上に高めかつ層状変形組織の各構成層の厚さを十分薄くすることが重視される場合またはその他の場合には、塑性変形を伴う強加工が加えられた材料を再度重ね合わせて出発材料として、さらに塑性変形を伴う強加工を加える。

上記の方法により、材料を有効に利用して大きな塑性変形を加えることが可能

となる。

上記の水素吸蔵材料の製造方法では、板や線の形状となつてからでは層状変形組織を形成しにくい場合またはその他の場合には、出発材料は粉末またはペレットの形態であり、延性を有したパイプ中に封入し、板や線の状態として強加工を行ったり、または塑性変形を伴うメカニカルアロイングによる強加工を実施する。

メカニカルアロイングにより粉末の状態では表面または内部まで層状変形組織が形成されるので、この粉末を用いて予備成形体を作製して所望の形状に加工することができる。この結果、形状の制約なしに、高い水素吸蔵能力と低い水素放出温度を兼備した部品を得ることが可能となる。

上記の水素吸蔵材料の製造方法では、塑性変形途中で温度が上がったり、また焼鈍したりする場合またはその他の場合においても、出発材料に選んだ材料の融点の80%以下の温度範囲で塑性変形を伴う強加工または焼鈍を加える。

温度が融点の80%を超えると、異種層の間で合金化が進行し、異種材料間の接触という趣旨が損なわれる。ここでの融点とは、一般に異種材料のうち高い融点を持つ材料の融点を意味するが、低融点材料内部へ高融点材料が選択的に拡散侵入する場合、合金化の進行を防止する観点から、拡散侵入の駆動力を低減するため、低融点材料の融点であってもよい。また、温度が融点の80%を超えると、転位や積層欠陥の密度が減少し、水素吸蔵能力が低下したり、水素の放出温度が低下しない。なお、融点は摂氏温度℃で表示し、上記の温度範囲はその摂氏温度℃の数値の80%以下の摂氏温度℃をさす。

発明を実施するための最良の形態

(実施例1：圧延加工)

まず、圧延加工によって本発明に係る層状変形組織を形成した実施例1について説明する。2A、3A、4A族金属のうちの1種類と6A、7A、8A族金属のうちの1種類との組み合わせは、表1の本発明例No. 1～12に示すものを用いた。2A、3A、4A族金属のうちの1種類を一の層、また6A、7A、8A族金属のうちの1種類を他の層と呼ぶが、一の層と他の層とは必ずしも交互に規則正しく配列されているわけではない。強加工のために一の層が切断された箇

2に示す組織は、試料端部等の加工度の高い箇所に認められる場合が多かったが、必ずしも加工度の高い箇所に限定されていない。本発明例の試料に認められる層状変形組織は、図3に示す従来の厚さの揃った整然とした構造と相違する。図3においては、積層構造101は、厚さの揃った、一の層102と、他の層103とからなる。厚さが揃い加工方向に揃って向いているが、このような整然さは必ずしも望ましいものではない。例えば、図2に示す構造では、全体として方向性が失われたために水素の移動速度は向上する。

本発明例No. 1～17の全てが2.0以上のH/Mを示した。No. 7～12およびNo. 15もH/Mは2.0以上を示した。なかでも、本発明例No. 2、5、7、9、14は、bcc構造を含まないにもかかわらず、高密度の欠陥を含むために、高いH/Mを示している。この理由は、上記したように、欠陥近傍に不純物が偏析しやすく、不純物の偏析によりその近傍では電荷の偏りが生じ、その偏りに水素原子がトラップされるからである。

実施例1のように強圧延加工を行った場合、結晶中に多数の欠陥が導入される。これら導入された欠陥は加工くり返し数の増加により欠陥が絡み合った状態へと変化する。これらの欠陥は、上記のように水素吸蔵能力を向上させるだけでなく、水素の高速拡散経路として作用し、水素の放出温度を低下させる。これら欠陥密度はX線回折ピークの半価幅によって評価される。ただし、ナノメートルオーダーの微細結晶材料では、その結晶粒子内に転位は存在しにくいと考えられるため、ここで言う欠陥密度とは必ずしも転位密度のみを表すものではない。水素の拡散速度を増大させるためには、半価幅は 0.2° 以上とする。さらに水素吸蔵量を増加させるためには、 0.5° 以上の半価幅を持つことが望ましい。表1に欠陥有りと表示した本発明例は、いずれも 1° 以上の半価幅を有するので、H/Mの向上に大きく寄与している。

また、表1の本発明例No. 5 (Mg/Ni (MgとNiとのモル比2:1)) について、上記した堀場製EMGA621により昇温分析を行い、水素放出速度を昇温速度 $10^{\circ}\text{C}/\text{分}$ の加熱条件にて求め、バルク材の Mg_2Ni と比較した。本発明例No. 5では、 50°C から水素の放出が認められ、 100°C で放出速度は最大となった。これに対して、バルク材の Mg_2Ni は $200\sim 300^{\circ}\text{C}$ の

範囲で水素の放出が行われた。したがって、上記のようにX線回折ピークの半価幅が 1° 以上となるような強加工を加え欠陥密度を高めることにより、本発明に係る水素吸蔵材料はニッケル水素2次電池や燃料電池用の水素供給源に実用的に利用されることが可能となる。この圧延による製造方法はイオンプレーティング法による製造方法と異なり、大量生産に適しており、トンオーダーの本発明に係る水素吸蔵材料を高い生産性のもとに製造することが可能である。

(実施例2：伸線加工)

まず、伸線加工によって本発明に係る層状変形組織を形成した実施例2について説明する。L系金属1種類とH系金属1種類との組み合わせは、表2の本発明例No. 1～12に示すものを用いた。また、H系金属のうちの2種類とL系金属のうちの1種類との組み合わせ等の実施例は、本発明例No. 13～17に示すものを用いた。ただし、本発明例No. 15はL系金属とH系金属との2種類の薄板からなり、L系金属としてMg-Si化合物（珪化マグネシウム）が用いられている。

表 2

		材料の 組合せ	組成比 (モル比)	水素吸蔵量 (H/M)	bcc 構造を示す XRD ピーク	欠陥
本 発 明 例	1	Ti/Cr	1:1	3.0	有	有
	2	Ti/Ni	2:1	2.5	無	有
	3	Ti/Fe	1:1	2.5	有	有
	4	Mg/Cr	2:1	2.5	有	有
	5	Mg/Ni	2:1	2.5	無	有
	6	Ca・Mg/Cr	1:1:2	2.5	有	有
	7	Y/Ni	1:1	2.0	無	有
	8	Y/Cr	1:1	2.5	有	有
	9	La/Ni	1:1	2.5	無	有
	10	La/Cr	1:1	2.5	有	有
	11	Yb/Ni	2:1	2.5	有	有
	12	Yb/Cr	2:1	2.5	有	有
	13	Cr/Mg/Ni	1:2:1	2.0	有	有
	14	Ti/Mg/Ni	1:1:1	2.0	無	有
	15	Mg-Si/Ni	2:1:1	2.0	有	有
	16	Mg/Cr/Ti	1:1:2	2.5	有	有
	17	Fe/Mg/Cr	1:1:1	2.0	有	有
比 較 例	18	MgNi ₅	- - - -	1.5	無	無
	19	CaNi ₅	- - - -	1.0	無	無
	20	LaNi ₅	- - - -	1.0	無	無
	21	LaCr ₅	- - - -	0.5	無	無

次に、表 2 の本発明例 No. 1 ～ 12 の試験体の製造方法について説明する。

L 系金属と H 系金属の粉末を、表 2 に示す各モル比に調整し、十分均一に混合した後、外径 20 mm、内径 16 mm の銅パイプの中に詰めた。各粉末の径の大きさは 1 mm 以下とした。この粉末の大きさは 50 μ m 以下とすることが望ましい。その後、銅パイプの端末を塞ぎ、伸線加工を行った。伸線加工はローラーダイスにより行ったが、スエージ加工、孔ダイスによる引き抜き、または圧延によっても可能である。伸線加工度は 1 パス当たりの減面率で 5 % ～ 30 % の範囲内で行い、トータル減面率は 96 % 以上とした。このトータル減面率は好ましくは 99.5 % 以上とする。伸線加工途中で 300℃ 以下の熱処理を施すと、より加工しやすく、また、粉末どうしの密着性が上がり密度が向上する。加工後、ワイヤの表面の銅を化学的処理または機械加工により除去して、L 系金属と H 系金属の混合体のワイヤを得た。これらワイヤを切り出し、水素吸蔵能 H/M を測定する水素試験体を採取した。また、ワイヤを複数本まとめて断面を切り出し樹脂に埋

めこみ研磨したX線回折用試験体を作製した。H/Mの測定法およびX線回折法は、実施例1と同様に行った。

表2に示す試験結果によれば、本発明例はH/Mが2.0以上と高い値を示した。これらのなかで、No. 2、5、7、9、14は、L系金属の層にbcc構造が含まれないにもかかわらず、高いH/M値となっている。これは、実施例1において詳述したように、高い欠陥密度に起因するものである。すなわち、本発明例では、X線回折ピークの半価幅は 1° 以上となっているので、転位や積層欠陥等が高密度で形成されている。これに対して、比較例のNo. 18~21のバルク材ではH/Mは0.5~1.5の範囲内にあり、しかもバルク材であるために水素の吸収と放出のくり返しサイクルによって微粉化しやすい。

上記の高欠陥密度の水素放出温度に及ぼす影響を把握するために、表2の本発明例No. 5について水素放出の調査を行った。調査方法は実施例1に記載したとおりである。その結果、表2の本発明例No. 5は、 50°C から水素放出を始め、 100°C で最大の放出速度を示すことが判明した。これに対して、バルク材の Mg_2Ni は $200\sim 300^{\circ}\text{C}$ の範囲で水素の放出が行われた。したがって、伸線加工によっても高密度の欠陥が水素吸蔵材料に導入され、水素放出温度を $100\sim 200^{\circ}\text{C}$ 低下させることが分かった。この結果、日常品に利用されるニッケル水素2次電池の電極や燃料電池用の水素供給源として使用することが可能となる。これらのワイヤはワイヤ状のまま、またはシート状等にされてニッケル水素2次電池の電極等に使用される。上記の伸線加工によれば、トンオーダーの本発明の水素吸蔵材料を高い生産性の下に製造することができる。

(実施例3：メカニカルアロイング)

Mgペレット、Niカーボニル粉末、金属クロム粉末を原料とし、あらかじめ最終組成比率の割合で、V型ミキサで予備混合後、Arガスが封入された遊星ボールミルで500時間メカニカルアロイング(MA)した。得られた粉末を金型を用いて500MPaの圧力で予備成形し、さらに 300°C に加熱した後、直ちに押出比10:1で押出し加工して、棒状の材料を得た。この実施の形態3においては、メカニカルアロイングの段階で各粉末の表層部には層状変形組織が形成され、さらに押出し加工により伸ばされ、押出し方向に延伸した各粉末が重なり

合って、層状変形組織が形成されている。なお、Mgの融点651℃、Niの融点1450℃、Crの融点1890℃なので、上記の300℃の加熱温度は各材料の融点の80%以下に十分収まっている。すなわち、Mgについて上記80%の温度は520.8℃であり、加熱温度300℃はこの温度より低い。

上記の棒状材料から水素試験体を採取して、実施例1と同様な方法によりH/Mおよび水素放出温度を測定した。本実施例3の試験体のH/Mは2.5であった。また、水素放出は50℃付近から始まり、80℃～100℃の範囲で放出速度は最大となり、100℃に到達した時点で吸蔵した水素の約80%が放出された。また、あらかじめ粉末から出発して微細化されているため、水素の吸蔵と放出のくり返しが行われても、水素吸蔵材の微細化は顕著に進行しなかった。

(実施例4：サイクリックプレス)

Mg薄板、Ni薄板およびCr薄板を素材として、あらかじめ最終組成比率を形成するように、それぞれの薄板を組み合わせで寸法を揃えて切断後、端部をスポット溶接で半固定した。その後、簡易金型中で加圧力800MPaで加圧し、得られた積層体を2分し、表面を清浄化した後、再度重ね合わせ加圧した。この加圧、切断、表面清浄化、プレス被加工材としての積層体の形成、のサイクルを1000回くり返し、層状変形組織を得た。

このサイクリックプレス法では、200回を超えるあたりから材料の硬化が始まった。そこで、1000回プレスをくり返した材料を純度99.99%の水素中で500℃で24時間保持して材料中の酸素の除去を行った。得られた材料の水素吸蔵量は、H/Mで3.0であったが、水素吸収温度および水素放出温度は室温から100℃の範囲内におさまリ、吸蔵量に対する放出量は80%以上であった。水素の吸収温度と放出温度が、室温から100℃の範囲内にすることができた理由として、水素との親和力が強いMgをNiとCrといった結晶構造の異なる材料で挟み込んだ結果、Mg中の結晶格子に大きな格子ひずみが発生し、水素とMgとの結合距離を広げたためと考えられる。なお、上記の水素焼鈍における加熱温度500℃は、Mgの融点651℃の80%の温度520.8℃より低い。

(実施例5)

実施例 4 と同じ加工用素材（出発材料）に対して、ロール圧延機で圧下率 20 %で圧延し、切断、表面清浄化、積層体形成、のくり返しを 1000 回くり返した。得られた試料を、純度 99.99 %の水素中で 500℃に加熱して 24 時間保持し、試料中の酸素の除去を行った。この試料の水素吸蔵量は、 H/M が 2.5 と高い値が得られた。水素吸収温度および水素放出温度は室温から 90℃の範囲内におさまリ、吸蔵量に対する放出量は 85 %以上であった。

水素の吸収温度および放出温度を室温から 90℃の範囲内とすることができた理由として、水素との親和力の強い Mg を Ni や Cr といった Mg と結晶構造が異なる材料で挟んだ結果、Mg の結晶格子に大きな格子ひずみが発生し、水素と Mg との結合距離を広げているためと考えられる。特に、ロール圧延の場合、加工に方向性が生じるために、Mg の結晶格子が加工方向に押し広げられている可能性がある。

本発明により、大量生産が可能な圧延加工等の方法により、高い水素吸蔵能力を有し、かつ水素放出温度が 100℃程度にまで低下した水素吸蔵材料を提供することができる。この結果、水素放出温度の低い水素吸蔵材料を多量に用いる自動車駆動用のニッケル水素 2 次電池の電極材料、燃料電池、および水素を利用したエネルギー変換システム等を始めとして、エネルギー関連産業における大規模な利用が可能となる。

上記において、本発明の実施例について説明したが、上記に開示した実施例は、あくまで例示であって、本発明の範囲はこれら実施例に限定されない。本発明の範囲は、特許請求の範囲の記載によって示され、さらに特許請求の範囲の記載と均等の意味および範囲内でのすべての変更を含む。

【図面の簡単な説明】

図 1 は、本発明の水素吸蔵材料に認められる一つの層状変形組織を示す模式図である。

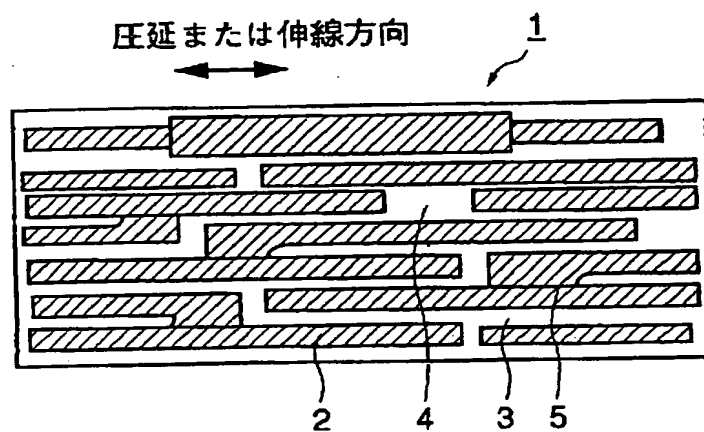
図 2 は、本発明の水素吸蔵材料に認められる他の層状変形組織を示す模式図である。

図 3 は、従来の積層構造を示す模式図である。

図 4 は、水素吸蔵処理を実現する装置の構成を示す模式図である。

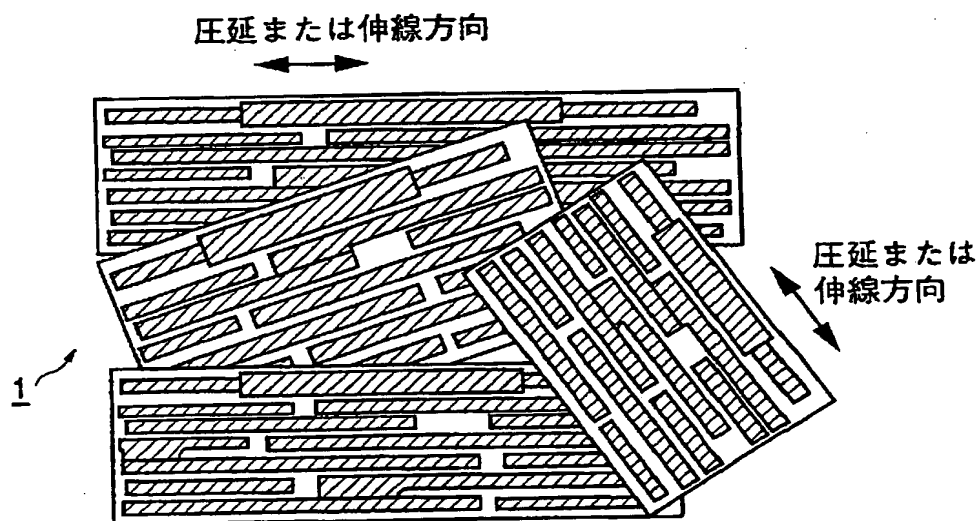
【図 1】

FIG. 1



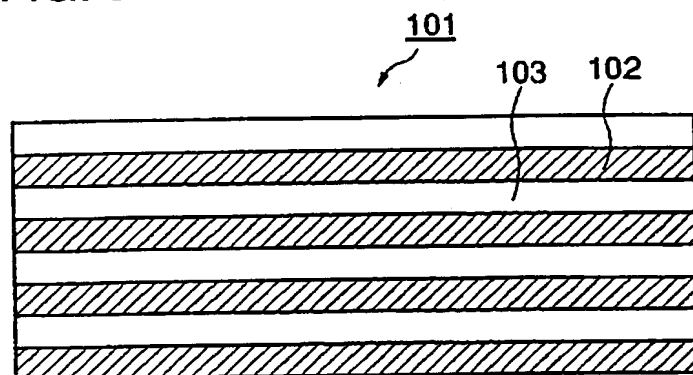
【図 2】

FIG. 2



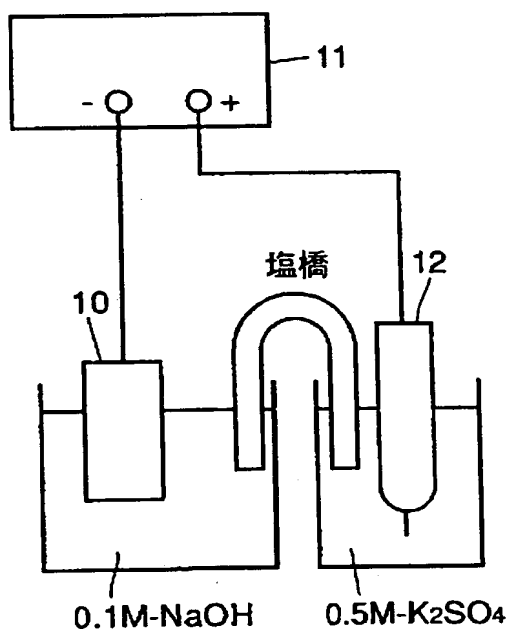
【圖 3】

FIG. 3



【圖 4】

FIG. 4



【国際調査報告】

国際調査報告		国際出願番号 PCT/JPO0/03710	
A. 発明の属する分野の分類 (国際特許分類 (IPC)) IntCl ¹ C22C 1/00, C01B3/00, B01J20/02, H01M4/38, 8/04, C23C14/14			
B. 調査を行った分野 調査を行った最小限資料 (国際特許分類 (IPC)) IntCl ¹ C22C 1/00, C01B3/00, B01J20/02, H01M4/38, 8/04, C23C14/14			
最小限資料以外の資料で調査を行った分野に含まれるもの 日本国実用新案公報 1925-1996年 日本国公開実用新案公報 1971-2000年 日本国特許実用新案公報 1994-2000年 日本国実用新案登録公報 1996-2000年			
国際調査で利用した電子データベース (データベースの名称、調査に利用した用語) WPI, CA, JOIS			
C. 関連すると認められる文献			
引用文献の カテゴリー*	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する 請求の範囲の番号	
X	バウンダリー, VOL. 12 NO. 4 P. 36-41 (1996)	1-4, 6-8	
Y	折茂茂一, 藤井博信 " 水素吸蔵合金の新しい展開 - ナノ複合化技術による高性能化 - "	5	
A	JP9-59001, A (住友電気工業株式会社), 4.3月. 1997, (04.03.97), 特許請求の範囲, (ファミリーなし)	1-8	
X	JPI-131001, A (三洋電機株式会社), 23.5月. 1989, (23.05.89), 特許請求の範囲, 第2頁左上欄第2行~右上欄第7行, (ファミリーなし)	1-5, 7, 8	
<input checked="" type="checkbox"/> C欄の続きにも文献が列挙されている。 <input type="checkbox"/> パテントファミリーに関する別紙を参照。			
* 引用文献のカテゴリー 「A」 特に関連のある文献ではなく、一般的技術水準を示すもの 「E」 国際出願日前の出願または特許であるが、国際出願日以後に公表されたもの 「L」 優先権主張に疑義を提起する文献又は他の文献の発行日若しくは他の特別な理由を確立するために引用する文献 (理由を付す) 「O」 口頭による開示、使用、展示等に言及する文献 「P」 国際出願日前で、かつ優先権の主張の基礎となる出願			
の日の後に公表された文献 「T」 国際出願日又は優先日後に公表された文献であって出願と矛盾するものではなく、発明の原理又は理論の理解のために引用するもの 「X」 特に関連のある文献であって、当該文献のみで発明の新規性又は進歩性がないと考えられるもの 「Y」 特に関連のある文献であって、当該文献と他の1以上の文献との、当業者にとって自明である組合せによって進歩性がないと考えられるもの 「&」 同一パテントファミリー文献			
国際調査を完了した日 01.09.00		国際調査報告の発送日 12.09.00	
国際調査機関の名称及びあて先 日本国特許庁 (ISA/JP) 郵便番号 100-8915 東京都千代田区霞が関三丁目4番3号		特許庁審査官 (権限のある職員) 小川 武 印 電話番号 03-3581-1101 内線 3435	

国際調査報告		国際出願番号 PCT/JPO0/03710
C (続き) . 関連すると認められる文献		
引用文献の カテゴリー*	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する 請求の範囲の番号
Y	JP7-54068, A(日本冶金工業株式会社), 28. 2月. 1995, (28. 02. 95). 特 許請求の範囲, (ファミリーなし)	5
A	JP51-148634, A(三菱重工業株式会社), 21. 12月. 1976, (21. 12. 76), 特許請求の範囲, 第 2 頁右上欄6-8行, (ファミリーなし)	1-8

フロントページの続き

(51) Int. Cl. 7	識別記号	F I		
H 0 1 M 4/38		H 0 1 M 4/38		A
8/04		8/04		J

(72) 発明者 武田 義信
兵庫県伊丹市昆陽北一丁目1番1号 住友
電気工業株式会社 伊丹製作所内

(72) 発明者 上村 卓
兵庫県伊丹市昆陽北一丁目1番1号 住友
電気工業株式会社 伊丹製作所内

(注) この公表は、国際事務局 (W I P O) により国際公開された公報を基に作成したものである。

なおこの公表に係る日本語特許出願 (日本語実用新案登録出願) の国際公開の効果は、特許法第184条の10第1項 (実用新案法第48条の13第2項) により生ずるものであり、本掲載とは関係ありません。